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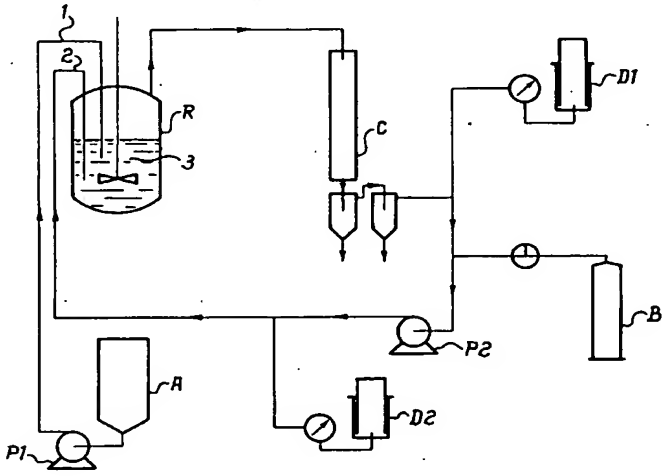
(54) Process for separating phthalimidoperoxycaproic acid (PAP) from solution(s) in organic solvents.

(57) Process for separating phthalimido-peroxycaproic acid (PAP) from solutions in organic solvents.
The process comprises the following steps:

- the solution of PAP in an organic solvent having a solubility in water which is a equal to, or lower than, 10% by weight, is fed to a reactor provided with a stirring system and containing an aqueous medium, through which a stream of air or inert gas is bubbled;
- the organic solvent is removed from the resulting suspension, kept with stirring;
- the evaporated solvent is recovered in a condenser system; and

PAP is recovered by filtering the suspension.



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The present invention relates to a process for separating phthalimido-peroxycaproic acid (PAP) from solutions in organic solvents in which it is dissolved.

In particular, the present invention relates to a process for separating phthalimido-peroxycaproic acid (PAP) from its solutions in chlorohydrocarbons used in order to prepare it, and from the solutions in the other organic solvents used for its subsequent purification.

The process for preparing PAP is known from European Patent Application No. 490,409.

According to this process, phthalimido-caproic acid (PAC) is converted into the peroxyacid, by H_2O_2, in the presence of a strong acid, in a double-phase system, in the presence of an organic solvent constituted by a halogenated aliphatic chlorohydrocarbon selected from dichloromethane and trichloromethane. The resulting PAP is recovered from the organic phase by low-temperature crystallization, or solvent removal under vacuum.

PAP recovered in that way can be purified by recrystallization or stripping, using organic solvents as disclosed in Italian Patent Application No. MI92-A-000 381 (filed on Feb. 21st, 1992).

The processes which apply the usual separation methods display some disadvantages; for example, the organic solvent used are not completely recyclable, owing to the accumulation of impurities, or unavoidable losses in the case of vacuum evaporation.

The present Applicant found now that the organic solvents can be re-used by means of a novel process used as an alternative to the usual separation methods, such as low-temperature crystallization or vacuum evaporation. This novel process makes it possible the process to be carried out under maximum safety conditions.

Therefore, the subject-matter of the present invention is a process for separating phthalimido-peroxycaproic acid (PAP) from solutions in organic solvents, characterized in that said process comprises the following steps:

-- the solution of PAP in an organic solvent having a solubility in water which is equal to, or lower than, 10% by weight (1), is fed to a reactor (R) containing an aqueous medium (3), through which a stream of air or inert gas (2) is bubbled;

-- the organic solvent is removed from the resulting suspension;

-- the evaporated solvent is recovered in a condenser system (C); and

-- PAP is recovered by filtering the suspension.

More particularly, the subject-matter of the present invention is a process for separating phthalimido-peroxycaproic acid (PAP) from solutions in organic solvents, characterized in that said process comprises the following steps:

-- the solution of PAP in an organic solvent having a solubility in water which is equal to, or lower than, 10% by weight (1), is fed to a reactor (R) equipped with a stirring system and containing an aqueous medium (3), through which a stream of air or inert gas (2) is bubbled, at a temperature comprised within the range of from +20 °C to 40 °C, and under a gauge pressure comprised within the range of from 0 to 0.266 bars (from 0 to 200 mm_{Hg});

-- the organic solvent is evaporated off from the resulting suspension, kept with stirring;

-- the evaporated solvent is recovered in a condenser system (C); and

-- PAP is recovered by filtering the suspension.

Following the feeding of organic PAP solution to the aqueous medium, a suspension is obtained which derives from the precipitation of PAP in the aqueous phase.

The ratio of the aqueous medium to suspended PAP is comprised within the range of from 6 to 15 by weight, preferably of from 8 to 12 by weight.

The temperature of the aqueous medium to which the PAP solution is fed is preferably comprised within the range of from +30 °C to 35 °C.

The gauge pressure inside the reactor (R) is preferably comprised within the range of from 0.133 to 0.2 bars (from 100 to 150 mm_{Hg}).

Exemplary organic solvents for PAP, having a solubility in water equal to, or lower than, 10% by weight, and from which the separation of PAP is carried out, are chlorohydrocarbons, such as, e.g., dichloromethane and trichloromethane, aliphatic esters, such as, e.g., methyl acetate and ethyl acetate.

The aqueous medium can be constituted by demineralized water, or aqueous solutions of inorganic salts, such as, e.g., Na_2SO_4, $MgSO_4$, $(NH_4)_2SO_4$. If an aqueous solution of inorganic salts is used, the solution can have a concentration comprised within a wide range, preferably of from 10 to 40%. The aqueous medium can contain small amounts (0.1-3%) of substances acting as acidity neutralizers, or metal ion sequestering agents, such as, e.g., sodium or potassium salts of citric, tartaric, phosphoric, phthalic acids, or NaOH, Na_2CO_3, and so forth.

The inert gas used in the process can be, e.g., N_2, CO_2, and their mixtures.

The solvents of PAP solutions are recovered according to the process of the present invention, in a system of condensers (C) kept at a temperature not lower than 0 °C, in order to prevent water entrained by the organic solvents, from solidifying. The system of condensers (C) continuously subtracts a portion of the organic solvents from the recycled gas, in such a way as to allow them to be completely recovered at the end of the operation.

According to the process of the invention, PAP is recovered by filtration from an aqueous medium, as a crystalline powder, or granular solid, and is subsequently washed with demineralized water and dried in a desiccator ($CaCl_2$).

A preferred form of practical embodiment of the process of the invention is illustrated in the flow scheme shown in the accompanying drawing. According to the drawing, an organic solution of phthalimido-peroxycaproic acid (PAP) (1), coming from the feed tank (A), is fed continuously, by means of a metering pump (P_1), to the aqueous medium (3) kept stirred inside the reactor (R). In the aqueous medium a gas stream (2) is caused to bubble. The gas is partially constituted by inert gas drawn at the beginning of the test, from the tank (B), and partially by not condensed vapours, continuously recycled by the pump (P_2). The solvent is recovered by means of a system of condensers (C) kept at a temperature higher than 0 °C (of round 5 °C). The hydraulic valves equipped with pressure gauges (D_1, D_2) are used in order to keep constant the pressure inside the equipment, preventing vapour leakages to the surrounding atmosphere.

The process according to the present invention can also be performed continuously. The stirred PAP suspension can be drawn continuously, and the aqueous medium and PAP can be refilled.

The PAP separated by means of this process is of good purity. Its purity is comprised within the range of from 96 to 99% by weight.

The process makes it possible the organic solvents to be recovered with a rate of 98% and at such a purity level that they can be used again in the subsequent processes for PAP separation or purification. In such a way, the process according to the present invention is a novel separation method and can be adopted jointly with the process for PAP preparation as disclosed in European Patent Application No. 490,409.

Furthermore, the process of the present invention makes it possible the steps in question to be carried out under maximal safety conditions, both avoiding environmental pollution problems and all those problems which are connected with possible risks of fires or explosions owing to the possible flammability of the used organic solvents.

In order to better understand the present invention and to practice it, some illustrative, non-limitative examples thereof are reported in the following.

Examples 1 - 3

A solution containing 400 g (18.8%) of PAP, 0.2% of H_2SO_4 and 80.5% of dichloromethane (deriving from the peroxidation process), was added to an aqueous medium, inside the reactor (R). The chlorinated solvent was removed through an air stream with vapours being recycled, and solvent vapours were condensed inside the system of condensers (C).

The operating conditions and the results obtained are reported in Table 1.

Example 4

A solution containing 400 g (12.31%) of PAP and 87.5% of ethyl acetate, was added to an aqueous medium, inside the reactor (R). The organic solvent (i.e., the ester) was removed by stirring the obtained suspension, causing an N_2 stream to bubble through the suspension, and by recycling the not condensed solvent vapours.

The operating conditions and the results obtained are reported in Table 1.

Examples 5 and 6 (Comparative Examples)

For comparison purposes, two tests were carried out in order to compare the separation methodology according to the present invention to the usual methodologies, such as, e.g., crystallization and vacuum evaporation.

A solution containing 400 g (18.8%) of PAP, and 80.5% of dichloromethane was submitted to crystallization at a temperature of -5 °C in Example 5. The solution (296 g), obtained after filtration, contained 94.1% of dichloromethane and 5.9% of impurities due to the presence of phthalimido-peroxycaproic (PAP) and phthalimido-caproic acid (PAC).

According to Example 6, the solvent of the solution containing 400 g (14.98%) of PAP and 84.8% of ethyl acetate was evaporated under vacuum in a rotational evaporator at a temperatue of 37 °C, under a residual pressure of 0.027 bars (20 mm_{Hg}).

The operating conditions and the results obtained are reported in Table 2.

The data reported in Tables 1 and 2 demonstrate that the usual methods make it possible a considerably lower recovery of organic solvents than as obtainable by means of the process of the invention. Furthermore, the crystallization supplies impurity-containing solvents.

Table 1

Example No.	Solution fed to purification: Used solvent: Type	Used solvent: Amount, g	PAP to be purified: Purity %	PAP to be purified: Chloroethanes, ppm	Operating conditions: Dissolution temperature °C	Stripping temperature °C	Residual pressure mmHg	Obtained PAP, as dry matter: Amount, g	Purity %	Chloroethanes, ppm	Residual solvent ppm
1	Methyl acetate	280	99.1	1,200	30°C	--	--	37.5	99.7	<1	690
2	Methyl acetate (H_2O)	260	99.1	1,200	30°C	35°C	100	49	99.2	3	750
3	Ethyl acetate	280	98.7	1,350	35°C	--	--	35.5	99.3	<1	890
3	Ethyl acetate	280	98.9	2,300	35°C	37°C	20	49	99.9	<1	400
4	Ethyl acetate + 4% (H_2O)	283	98.5	1,730	25°C	--	--	35.5	99.3	2	650
4	Ethyl acetate (H_2O)	283	98.5	1,730	25°C	35°C	60	48.5	98.6	<1	480

Table 2

Example No.	Solution fed to purification				Operating conditions			Obtained PAP, as dry matter			
	Used solvent		PAP to be purified		Dissolution temperature °C	Stripping temperature °C	Residual pressure mbar	Amount, g	Purity %	Chloromethanes, ppm	Residual solvent ppm
	Type	Amount, g	Purity %	Chloromethanes, ppm							
5	Ethanol	150	98.8	1,900	35°C	--	--	38	99.5	<1	680
5	Ethanol	200	98.5	1,730	35°C	37°C	20	49	98.4	<1	590
6	Acetone	188	98.5	950	30°C	--	--	30	99.2	2	630
6	Acetone	188	98.5	950	30°C	37°C	20	49.5	98.6	<1	370

Claims

1. Process for separating phthalimido-peroxycaproic acid (PAP) from solutions in organic solvents, in which it is dissolved, characterized in that said process comprises the following steps:

-- the solution of PAP in an organic solvent having a solubility in water which is equal to, or lower than, 10% by weight (1), is fed to a reactor (R) containing an aqueous medium (3), through which a stream of air or inert gas (2) is bubbled;
-- the organic solvent is removed from the resulting suspension;
-- the evaporated solvent is recovered in a condenser system (C); and
-- PAP is recovered by filtering the suspension.

2. Process according to claim 1, characterized in that the reactor is equipped with a stirring system and is kept at a temperature comprised within the range of from +20 °C to 40 °C and under a gauge pressure comprised within the range of from 0 to 0.266 bars (from 0 to 200 mm_{Hg}) and in that the organic solvent is removed from the suspension, kept stirred, by evaporation, and PAP is recovered by filtration.

3. Process according to claim 1 or 2, characterized in that the ratio of the aqueous medium to suspended PAP is comprised within the range of from 6 to 15 by weight.

4. Process according to claim 3, characterized in that the ratio is preferably comprised within the range of from 8 to 12.

5. Process according to any of the preceding claims, characterized in that the aqueous medium is demineralized water.

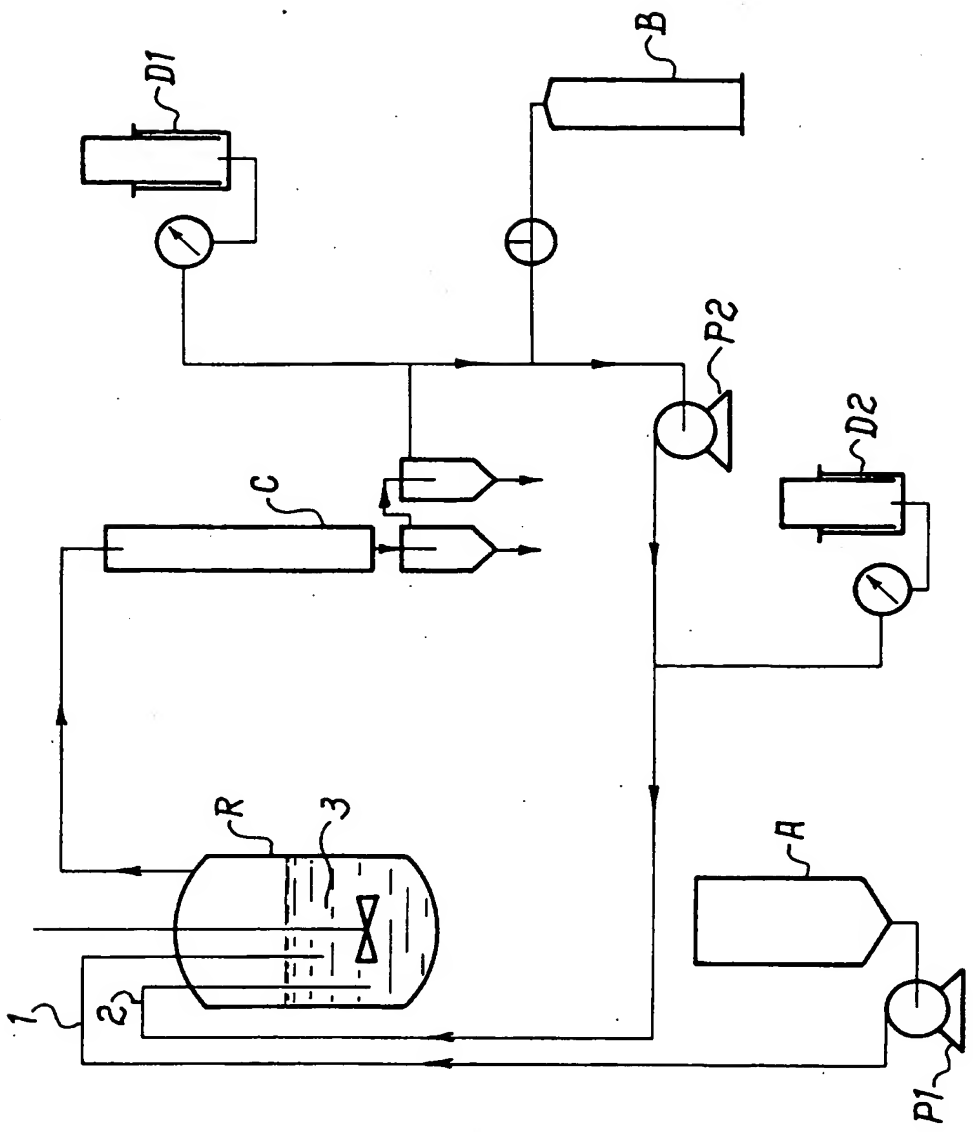
6. Process according to any of the preceding claims, characterized in that the aqueous medium is an aqueous solution of inorganic salts.

7. Process according to claim 6, characterized in that the inorganic salts are selected from Na_2SO_4, $MgSO_4$, $(NH_4)_2SO_4$ or mixtures thereof.

8. Process according to any of the preceding claims, characterized in that the inert gas preferably is N_2, CO_2 or mixtures thereof.

9. Process according to any of the preceding claims, characterized in that the temperature is preferably comprised within the range of from +30 °C to 35 °C.

10. Process according to any of the preceding claims, characterized in that the gauge pressure preferably is comprised within the range of from 0.133 to 0.2 bars (from 100 to 150 mm_{Hg}).


D1
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EUROPEAN SEARCH REPORT

Application Number
EP 93 10 3207

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	FR-A-2 385 697 (FMC CORPORATION) 27 October 1978 * claims 1,5 *	1-10	C07D209/48
D,Y, P	EP-A-0 490 409 (AUSIMONT S.P.A.) 17 June 1992 * claim 1 *	1-10	
A	EP-A-0 325 288 (AUSIMONT S.R.L.) 26 July 1989 * claim 6 *	1-10	
A	WO-A-9 007 501 (INTEROX CHEMICALS LTD.) 12 June 1990 * claim 2 *	1-10	
A	DE-A-3 823 172 (HOECHST AG) 11 January 1990 * claim 1 *	1-10	
A	DE-A-4 003 309 (HOECHST AG) 8 August 1991 * claim 1 *	1-10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	WO-A-9 014 336 (INTEROX CHEMICALS LTD.) 29 November 1990 * claim 1 *	1-10	C07D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	30 APRIL 1993	GETTINS M.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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